brine causes a driving force for transport of $Mg^{2+}$ ions from the feed into the brine. Countercurrent operation allows the large driving force to be maintained over the length of the membrane.

A hollow-fibre device has been used as a suppressor for ion chromatography. Compared to an ion-exchange column that is normally used to suppress conductance in the eluant, Donnan dialysis allowed more control over the conductivity and eliminated the need to regenerate the resins. Moreover, the resolution was improved by the use of Donnan dialysis.

The use of neutralization dialysis for desalination of cheese whey has been described.

## Conclusion

Donnan dialysis can be used in many applications where ion-exchange beads are currently applied. The process might find a niche in water softening in a capacity range between that of home water softeners and the large-scale lime-soda softeners. Capital costs are higher for membranes than for resin beads, but the use of membranes offers the advantages of steady-state operation without the need for rinse-down, which produces large volumes of water that must be discarded. The capital cost of small-scale Donnan dialysis could be reduced by the availability of more ion-exchange membranes in hollow-fibre form that could be assembled into compact modules.

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# Electrodialysis

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Electrodialysis is a process in which ion exchange membranes in combination with an electrical potential difference are used to remove ionic species from an aqueous solution. The large scale industrial utilization of the process began about 30 years ago with the development of highly selective ion exchange membranes of low electric resistance arranged in a multicell stack.

Until the mid 1970s electrodialysis stacks were operated in a unidirectional mode, that is, the polarity of the electrodes was fixed. A significant step towards the efficient application of electrodialysis was the introduction of a new mode of operation referred to as electrodialysis reversal. In this operating mode the flow streams and the polarity in an electrodialysis stack are periodically reversed, which reduces membrane fouling and scaling. Costly and time-consuming membrane cleaning procedures are then unnecessary.

The main application of electrodialysis is the desalination of brackish water for domestic and industrial use. In Japan electrodialysis is also used on a large scale to concentrate sodium chloride from sea water for the production of table salt. More recently

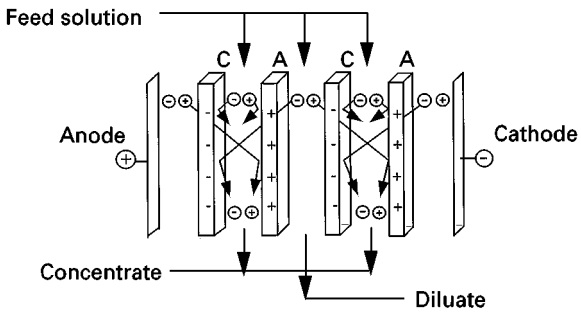


**Figure 1** Schematic diagram illustrating the principle of electrodialysis.

utilization of electrodialysis in the food and chemical industry and to treat certain industrial effluent streams has become important.

## The Principle of Electrodialysis

The principle of electrodialysis is illustrated in **Figure 1**. A typical electrodialysis cell arrangement consists of a series of anion and cation exchange membranes arranged in an alternating pattern between an anode and a cathode to form individual cells. If an electrolyte solution is passed through these cells and an electrical potential is established between the electrodes, the positively charged cations migrate towards the cathode and the negatively charged anions towards the anode. The positively charged cations can easily permeate the negatively charged cation exchange membrane but are retained by the positively charged anion exchange membrane. Likewise, negatively charged anions permeate the anion exchange membrane but are retained by the cation exchange membrane. The overall result is an increase in the ion concentration in alternate compartments, while the other compartments simultaneously become depleted. The depleted solution is referred to as diluate and the concentrated solution as brine or concentrate. The driving force for the ion transport in the electrodialysis process is the applied electrical potential. The total space occupied by the diluate and the concentrated solutions and the contiguous anion and cation exchange membranes make up a cell pair. The cell pair is the repeating unit in an electrodialysis stack.

## The Ion Exchange Membranes

Ion exchange membranes are the key components in electrodialysis. They consist of highly swollen gel-type polymer structures carrying fixed positive or negative charges. Polymer structures carrying negatively charged groups are referred to as cation exchange membranes, while those carrying positively charged groups are referred to as anion exchange membranes.

In a cation exchange membrane, the fixed negative charges are in electrical equilibrium with mobile cations in the interstices of the polymer. **Figure 2** shows a cation exchange membrane with fixed anions and mobile cations; the latter are referred to as counter ions. The mobile anions, called co-ions, are more or less completely excluded from the polymer matrix because their electrical charge is identical to that of the fixed ions. Because of the exclusion of the co-ions, cation exchange membranes are preferentially permeable for cations. Anion exchange membranes which carry positive fixed charges and exclude cations are preferentially permeable to anions. The extent to which co-ions are excluded from an ion exchange membrane depends on the membrane as well as on the solution properties.

The most desirable properties for ion exchange membranes are:

- High permselectivity – the membrane should be permeable to counter-ions only
- Low electrical resistance – the membrane should have high counter ion permeability
- Good mechanical and form stability – the membrane should be mechanically strong and should have a low degree of swelling in diluate solutions
- High chemical stability – the membrane should be stable over the entire pH range and in the presence of oxidizing agents and organic solvents.

The properties of ion exchange membranes are determined by the base polymer and the type and concentration of the fixed charges. The base polymer determines the mechanical, chemical and thermal

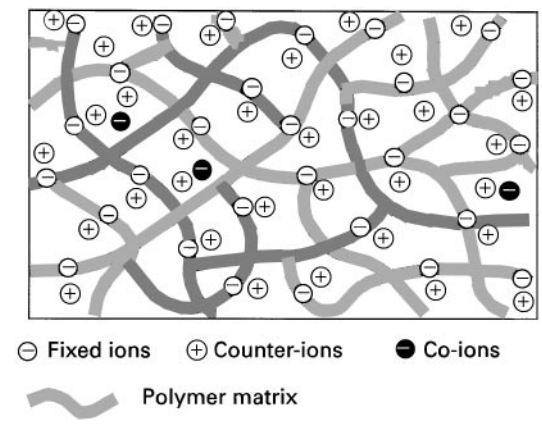


**Figure 2** Schematic drawing illustrating the structure of a cation exchange membrane.

stability of the membrane. The type and concentration of the fixed ions determine the permselectivity and the electrical resistance. The moieties often used as fixed charges are $-SO_3^-$ and $-COO^-$ groups in cation exchange membranes and $-R_3N^+$ and $-R_2NH^+$ groups in anion exchange membranes. The sulfonic acid group $-SO_3^-$ is completely dissociated over the entire pH range, while the carboxylic acid group $-COO^-$ is virtually undissociated in the pH range $< 3$. The quaternary ammonium group $-R_3N^+$ again is completely dissociated over the entire pH range, while the tertiary ammonium group $-R_2NH^+$ is only weakly dissociated. Accordingly, ion exchange membranes are referred to as weakly or strongly acidic or basic in character depending on the charged groups they contain.

## Mass Transfer in Electrodialysis

Mass transfer in electrolyte solutions is determined by the driving forces acting on the individual ions of the solution and by the friction of the ions with other components in the solution. The driving forces can be expressed by gradients in the electrochemical potential of individual components. The friction that has to be overcome by the driving force can be expressed by the ion mobility or diffusivity.

To describe the mass transport in a system, thermodynamic and kinetic parameters must be mathematically related. Several relations are described in the literature. The one most frequently used is the Nernst–Planck equation which describes transport of ions under isobaric and isothermal conditions in an ion exchange membrane as follows:

$$J_i = m_i C_i \frac{d\eta_i}{dz} = m_i C_i \left( z_i F \frac{d\varphi}{dz} + \frac{d\mu_i}{dz} \right)$$

$$= m_i C_i \left( z_i F \frac{d\varphi}{dz} + RT \frac{d \ln a_i}{dz} \right) \qquad [1]$$

For the definition of symbols in this and all other equations, see **Table 1**. $J_i$ is the flux in the direction perpendicular to the membrane surface and $z$ refers to the number of charges carried by an ion and indicates whether these charges are positive or negative.

A boundary condition for describing the mass transport in electrolyte solutions is the electroneutrality requirement which postulates that on a macroscopic scale there is no excess in positive or negative charges. Thus:

$$\sum_i z_i C_i = 0 \quad (i = 1, 2, 3 \ldots n) \qquad [2]$$

The concentration of individual ions is related to that of the salt by the stoichiometric coefficient $\nu$ which determines into how many ions a salt will dissociate in the solution. Thus:

$$C_i = \nu_i C_s \qquad [3]$$

Another assumption in electrodialysis is that electrical charges are transported exclusively by ions. Thus:

$$I = \sum_i z_i F J_i \qquad [4]$$

Here $J_i$ is the flux of the individual ions and $I$ is the total electrical current.

### Transport and Transference Numbers

The transport number $T_i$ and the transference number $t_i$ of an ion $i$ are given by:

$$T_i = \frac{z_i J_i}{\sum_i z_i J_i} \quad \text{and} \quad t_i = \frac{T_i}{z_i} = \frac{J_i}{\sum_i z_i J_i} \qquad [5]$$

Here $T_i$ indicates the fraction of the total current carried by the ion $i$, and $t_i$ determines the number of moles of the ion $i$ transported per mole of electrons, i.e. per Faraday.

The transference number is directly related to the ion concentration and their mobility and its sum is 1. Thus:

$$t_i = \frac{C_i m_i}{\sum_i z_i C_i m_i} \quad \text{and} \quad \sum_i t_i = 0 \qquad [6]$$

The transference numbers of different salt ions in solution are not very different. In an ion exchange membrane, however, there are the fixed ions of the membrane in addition to the mobile ions of the electrolyte. The fixed ions do not contribute to the transport of electrical charges. Their transference number is therefore 0. Furthermore, the concentration of the counterions is much lower than that of the co-ions. Their concentration in the membrane determines the permselectivity of a membrane.

### Membrane Permselectivity

The permselectivity of cation and anion exchange membranes is defined by:

$$\psi^{mc} = \frac{t_c^{mc} - t_c}{t_a} \quad \text{and} \quad \psi^{ma} = \frac{t_a^{ma} - t_a}{t_c} \qquad [7]$$

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**Table 1** Definition of symbols used in mathematical equations

| *Symbol* | *Definition* |
|---|---|
| $\eta$ | Electrochemical potential |
| $\mu$ | Chemical potential |
| $\varphi$ | Electrical potential |
| $\nu$ | Stoichiometric coefficient which determines into how many ions a salt will dissociate in the solution |
| $\psi$ | Permselectivity of a membrane |
| $\xi$ | Current utilization |
| $\Delta$ | Thickness of a cell |
| $\rho$ | Resistance of ion exchange membranes |
| $\Delta\varphi$ | Potential difference between solutions separated by a membrane assuming electrochemical equilibrium |
| $\Delta C$ | Difference in salinity of feed and product water |
| $\varphi_{Don}$ | Donnan potential |
| $\Delta G$ | Energy required for production of the dilute |
| $\gamma_{\pm}^{m}$ | Average activity coefficients of salt in the membrane |
| $\Delta n_s$ | Amount of salt in moles transferred from a feed to a concentrate solution |
| $\Delta p$ | Hydrodynamic pressure loss through the stack |
| $\Lambda_s$ | Equivalent conductivity |
| $\gamma_{\pm}^{s}$ | Average activity coefficients of salt in the electrolyte solution |
| $\Delta z$ | Thickness of the boundary layer |
| $a$ | Activity |
| $A$ | Effective area |
| $A_{min}$ | Minimum membrane area required for a certain plant capacity |
| $\Delta C$ | Concentration differences between feed and diluate |
| $C_{co}^{m}$ | Co-ion concentration in the membrane |
| $C_{f}^{m}$ | Concentration fixed ions in the membrane |
| $C_{co}^{s}$ | Co-ion concentration in the electrolyte solution |
| $D$ | Diffusion coefficient |
| $dz$ | Directional coordinate perpendicular to the membrane surface |
| $E_{des}$ | Energy required for desalination |
| $E_p$ | Pumping energy |
| F | Faraday constant |
| $I$ | Total electrical current |
| $i$ | Current density |
| $i_{lim}$ | Limiting current density |
| $J_i$ | Flux of component *i* (individual ions) |
| k | Constant referring to efficiency of pumps |
| $m$ | Mobility of ions in the membrane |
| $n$ | Number of cell pairs in a stack |
| $Q$ | Volumetric flow of the product |
| R | Gas constant |
| $R$ | Electric resistance |
| $T$ | Temperature |
| $t$ | Transference number |
| $t$ | Time |
| $T_i$ | Transport number of component *i* (ions) |
| $u$ | Linear flow velocity of solution in electrodialysis cells |
| $U$ | Voltage drop across the electrodialysis stack |
| $V$ | Volume |
| $z$ | Electrochemical valence |
| **Superscripts** | |
| $'$ and $''$ | Two phases separated by the membrane |
| b | Boundary layer |
| ba | Concentrate bulk solution |
| bc | Concentrate bulk solution |
| bd | Diluate solution in the bulk |
| diff | Ion diffusion |
| l | Current leakage through the manifold |
| m | Membrane |
| ma | Anion membrane |
| mc | Cation membrane |
| md | Diluate solution at the membrane surface |
| mig | Ion migration |
| ms | Membrane selectivity |
| o | Feed |
| p | Product solution |
| s | Solution |
| sc | Concentrate solution |
| sd | Diluate concentration |
| se | Electrode rinse solution |
| sf | Feed solution |
| sp | Product solution |
| w | Water transport through the membranes |
| **Subscripts** | |
| a | Anion |
| c | Cation |
| cou | Counterion |
| i | Ion |
| s | Salt |
| w | Water |

The permselectivity of an ion exchange membrane relates the transport of electric charges by counterions to the total transport of electric charges through the membrane. An ideal permselective cation exchange membrane would transmit positively charged ions only, i.e. for $t_c^{mc} = 1$, $\psi^{mc} = 1$. The permselectivity approaches zero when the transference number within the membrane is identical to that in the electrolyte solution. For the anion exchange membrane the corresponding relationship holds.

### Diffusion Potential, Donnan Equilibrium and Ion Exclusion

The diffusion potential can be derived by integration of eqn [1] and is given for a monovalent electrolyte when the ion activity is expressed by the salt concentration by:

$$\Delta\varphi = \varphi' - \varphi'' = \frac{RT}{F}\left(\frac{m_a - m_c}{m_a + m_c}\right)\ln\frac{C_s'}{C_s''} \qquad [8]$$

An electrical potential difference is not only established between two solutions of different concentrations separated by a membrane but also between a membrane and the adjacent electrolyte solution if the ion concentration in the membrane is different from that in the adjacent solution,

which is generally the case with ion exchange membranes. This potential difference is referred to as the Donnan potential.

The Donnan potential cannot be measured directly. It can, however, be calculated from the electrochemical equilibrium of ions between the membrane and the adjacent solution. By introducing the proper relations for the electrochemical potential, the Donnan potential – the electrical potential difference between an ion exchange membrane and a solution of a monovalent salt – can be calculated to a first approximation by:

$$\Delta\varphi_{\mathrm{Don}} = \varphi^{\mathrm{m}} - \varphi^{\mathrm{s}} = \frac{RT}{F}\ln\frac{a_{\mathrm{i}}^{\mathrm{m}}}{a_{\mathrm{i}}^{\mathrm{s}}} \qquad [9]$$

The numerical value of $\Delta\varphi_{\mathrm{Don}}$ is negative for the cation exchange membrane and positive for the anion exchange membrane in equilibrium with a dilute electrolyte solution.

The Donnan potential is also the basis for calculating the Donnan exclusion, which determines the co-ion concentration in a membrane. For a monovalent electrolyte, i.e. $z_{\mathrm{i}} = 1$, and assuming a high fixed ion concentration in the membrane compared to the electrolyte concentration, the co-ion concentration in the membrane is given to a first approximation by:

$$C_{\mathrm{co}}^{\mathrm{m}} = \frac{C_{\mathrm{co}}^{\mathrm{s}^2}}{C_{\mathrm{f}}^{\mathrm{m}}}\left(\frac{\gamma_{\pm}^{\mathrm{s}}}{\gamma_{\pm}^{\mathrm{m}}}\right)^2 \qquad [10]$$

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## Energy Requirements in Electrodialysis

The energy required in an electrodialysis process is the sum of two terms: firstly, the electrical energy needed to transfer the ionic components from a feed solution through the membranes into the concentrate solution, and secondly, the energy required to pump the solutions through the electrodialysis unit. Energy consumption due to electrode reactions can generally be neglected because of the large number of cell pairs usually stacked between the two electrodes.

### Minimum Energy Required for Transfer of Ions from a Feed to a Concentrate Solution

In electrodialysis the minimum energy required for the transport of salt from a feed to a concentrate solution can be expressed by the Gibbs free energy of mixing. Taking into account the electrolyte concentrations in the feed, diluate and concentrate, the minimum desalting energy is given by:

$$\Delta G = z\mathrm{R}\mathrm{T}\Delta n_{\mathrm{s}}\left[\frac{\ln\dfrac{C_{\mathrm{s}}^{\mathrm{sf}}}{C_{\mathrm{s}}^{\mathrm{sc}}}}{\dfrac{C_{\mathrm{s}}^{\mathrm{sf}}}{C_{\mathrm{s}}^{\mathrm{sc}}} - 1} - \frac{\ln\dfrac{C_{\mathrm{s}}^{\mathrm{sf}}}{C_{\mathrm{s}}^{\mathrm{sd}}}}{\dfrac{C_{\mathrm{s}}^{\mathrm{sf}}}{C_{\mathrm{s}}^{\mathrm{sd}}} - 1}\right] \qquad [11]$$

### Practical Energy Requirements in Electrodialysis

As discussed previously, the minimum energy required for desalting a given feed solution refers to a reversible process. In electrodialysis there are also irreversible energy losses and the total electric energy required for the transfer of ions from a feed solution to a concentrate, i.e. the actual energy used for desalination is much larger than the theoretical minimum value. This is given by:

$$E_{\mathrm{des}} = UIt = RI^2t \qquad [12]$$

The electric current required for the desalination of a feed solution is directly proportional to the concentration difference between the feed and the diluate solution. It is given by:

$$I = \frac{V^{\mathrm{p}}|z_{\mathrm{a}}||z_{\mathrm{c}}|\nu_{\mathrm{s}}\mathrm{F}(C_{\mathrm{s}}^{\mathrm{sf}} - C_{\mathrm{s}}^{\mathrm{sp}})}{\xi t} \qquad [13]$$

The current utilization is the fraction of the total current passing through the electrodialysis stack that is used for the transfer of ions. It will be discussed in more detail later.

The electrical resistance of an electrodialysis stack is determined by the resistances of the membrane and diluate and concentrate solutions and is given to a first approximation by:

$$R = \frac{U}{I} = \frac{n}{A}\left[\frac{2\Delta}{\Lambda_{\mathrm{s}}}\left(\frac{1}{C_{\mathrm{s}}^{\mathrm{sd}}} + \frac{1}{C_{\mathrm{s}}^{\mathrm{sc}}}\right) + \rho^{\mathrm{ma}} + \rho^{\mathrm{mc}}\right] \qquad [14]$$

The electrical resistance of the solutions is inversely proportional to their salt concentrations, which are changing while passing through the stack from the feed to the product concentration. The concentration in the diluate cell is decreasing and that in the concentrate cell increasing. An electrical resistance of a stack can thus be calculated as a function of the cell thickness, i.e. the distance between two membranes. Generally, the resistances of the ion exchange membranes and the average resistance of the concentrate solution are much lower than the average resistance of the diluate and can therefore be neglected.

The electrical resistance of a stack can be calculated to a first approximation from the integral

average of the diluate concentration and is given by:

$$R = \frac{n}{A}\left[\frac{\Delta \ln \frac{C_s^{sf}}{C_s^{sp}}}{\Lambda_s(C_s^{sf} - C_s^{sp})}\right] \qquad [15]$$

The superscripts sf and sp refer to the feed and the diluate at the cell outlet, which is the required product.

A combination of eqns [13] and [15] gives the energy required to remove a certain amount of salt from a feed solution. For the desalination of a monovalent salt, i.e. where $z_a$, $z_c$ and $\nu_s$ are all unity, the electrical energy is given by:

$$E_{des} = \frac{n}{A}\frac{V^{p^2}F^2(C_s^{sf} - C_s^{sp})}{\xi}\left[\frac{\Delta \ln \frac{C_s^{sf}}{C_s^{sp}}}{\Lambda_s}\right] \qquad [16]$$

For a given plant capacity, salt solution and cell design, the equivalent conductivity and the number and area of cells are constant. Thus, the energy required for the desalination of a monovalent salt solution can be expressed to a first approximation by the constant factor $k$, by the current utilization and by the feed and the product concentration.

$$E_{des} = \frac{k}{\xi}(C_s^{sf} - C_s^{sp}) \log \frac{C_s^{sf}}{C_s^{sp}} \qquad [17]$$

### Pumping Energy Requirements

The operation of an electrodialysis unit requires one or more pumps to circulate the diluate, the concentrate and the electrode rinse solution through the stack. The energy required for pumping these solutions is determined by the volumes to be circulated and the pressure drop. It can be expressed by:

$$E_p = k(V\Delta p^{sd} + V^{sc}\Delta p^{sc} + V^{se}\Delta p^{se}) \qquad [18]$$

## Processes Affecting the Efficiency of Electrodialysis

In practical application electrodialysis is effected by concentration polarization and by incomplete current utilization. Both phenomena influence the efficiency of the process.

### Current Utilization

Current utilization in an electrodialysis stack is impaired by incomplete membrane selectivity, parallel current through the stack manifold and water transfer across the membranes due to osmosis and electroosmosis.

The ratio of the actual current needed for salt transport from a feed to a concentrate stream to that calculated theoretically is referred to as the current efficiency, which for one cell pair is given by:

$$\eta = \eta^{ms}\eta^{w}\eta^{l} \qquad [19]$$

The efficiency term $\eta^{ms}$ is a function of the membrane permselectivities. $\eta^{w}$ is caused by convective flow due to the hydrostatic pressure difference between the diluate and concentrate cells, by transfer of water in the hydration shell of ions and by osmosis. $\eta^{l}$ is determined by parallel current through the stack manifold.

The overall current utilization $\xi$ can be defined as a function of the number of cell pairs, membrane selectivity, water transfer and manifold current flow. It is given by:

$$\xi = n(\psi^{mc}t_a + \psi^{ma}t_c)\,(1 - [t_w^{mc} + t_w^{ma}]) \times 0.018(C_s^{sc} - C_s^{sd})\eta^{l} \qquad [20]$$

For relatively dilute solutions, $C_s < 0.1\ \text{mol L}^{-1}$, the efficiency loss due to water transfer is quite low. However, for higher feed solution salt concentrations the water transfer may affect the efficiency of electrodialysis quite significantly.

The current leakage through the manifold system can, in a well-designed stack, be neglected, i.e. $\eta^{l} \approx 1$.

### Concentration Polarization and Limiting Current Density

Concentration polarization occurs in all mass separation processes and is the result of changes in mass transport properties at an interface. In electrodialysis, separation of ions is the result of differences in their transport numbers in solution and in the membranes. At the surface of an ion exchange membrane facing the diluate the concentration of counterions is reduced and at the surface facing the concentrate the concentration of counterions is increased because of the lower transport number of the counterions in the solution than that in the membrane. Because of the electroneutrality requirement, the co-ions in the boundary layers are transported in the opposite direction. Thus, salt concentration gradients are established in the boundary layers at membrane surfaces, which leads to an additional mass transport towards the membrane surface in the diluate and away from it in the concentrate solution. Due to turbulent mixing

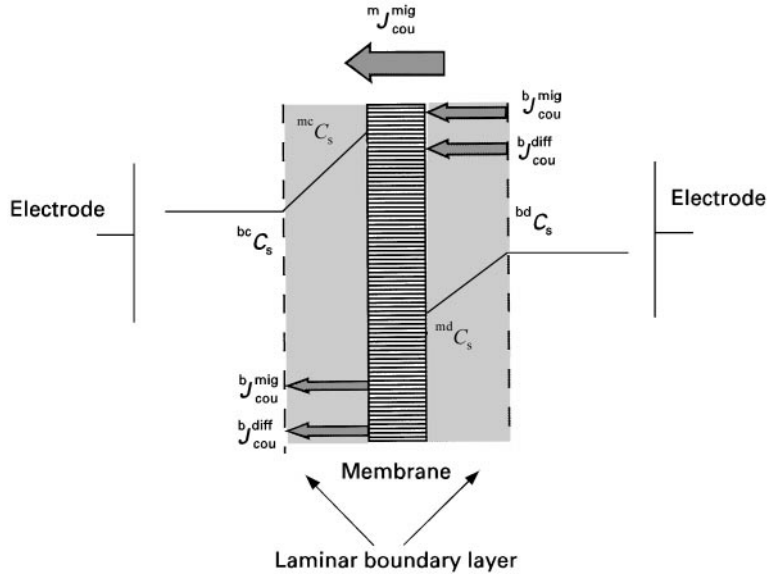


**Figure 3** Schematic drawing illustrating concentration profiles of a salt in the boundary layer on both sides of an ion exchange membrane and the fluxes of cations and anions in the boundary layer and the membrane surface. For abbreviations, see Table 1.

of the bulk solutions, the concentration gradients are limited to a relatively thin laminar boundary layer at the membrane surfaces, as indicated in **Figure 3**, which shows the salt concentration profiles in the solutions near the surface of an anion exchange membrane.

The concentration profiles at the membrane surface can be determined by a mass balance based on the so-called Nernst film model, which assumes static boundary layers at the membrane surfaces, where concentration and electrical potential gradients perpendicular to the membrane surfaces are the only driving forces for the mass transport. The bulk solution between the laminar boundary layer is well mixed and has a uniform concentration. It can be assumed that the transport of ions through an ion exchange membrane is the result of migration caused only by an electrical potential gradient, while in the solution ions are transported by both migration and diffusion. In a steady state the ion flux through the membrane is identical to that through the boundary layer. For a strictly permselective membrane it is given by:

$$ {}^{m}J_{cou}^{mig} = -{}^{b}J_{cou}^{mig} + {}^{b}J_{cou}^{diff} = t_{cou}^{m}\frac{i}{F} = t_{cou}^{b}\frac{i}{F} - D_s\frac{dC_s}{dz} \quad [21] $$

The current density can be obtained from eqn [21] by integration over the boundary layer. For the boundary layer at the membrane surfaces adjacent to the diluate the current density is:

$$ i = -\frac{FD_s}{(t_{cou}^{m} - t_{cou})}\frac{{}^{bd}C_s - {}^{md}C_s}{\Delta z} \quad [22] $$

When the hydrodynamic flow conditions are kept constant the boundary layer thickness, $\Delta z$, will be constant and the current will reach a maximum value independent of the electrical potential gradient if the salt concentration at the membrane surface, ${}^{md}C_s$, becomes 0. This maximum current is referred to as the limiting current density, $i_{lim}$, which is given by:

$$ i_{lim} = -\frac{FD_s}{(t_{cou}^{m} - t_{cou})}\frac{{}^{bd}C_s}{\Delta z} \quad [23] $$

Exceeding the limiting current density in practical applications of electrodialysis can affect the efficiency of the process severely by increasing the electrical resistance of the solution and by causing water splitting, which leads to changes in the pH values of the solutions, causing precipitation of metal hydroxides on the membrane surface.

## Electrodialysis Process and Equipment Design

The performance of electrodialysis in practical applications is not only a function of membrane properties but is also determined by the membrane stack and the overall process design.

### Electrodialysis Stack Design

Two different stack designs are used in large scale applications today. One is the so-called sheet flow and the other is the tortuous path flow design. A typical sheet flow electrodialysis stack is shown in

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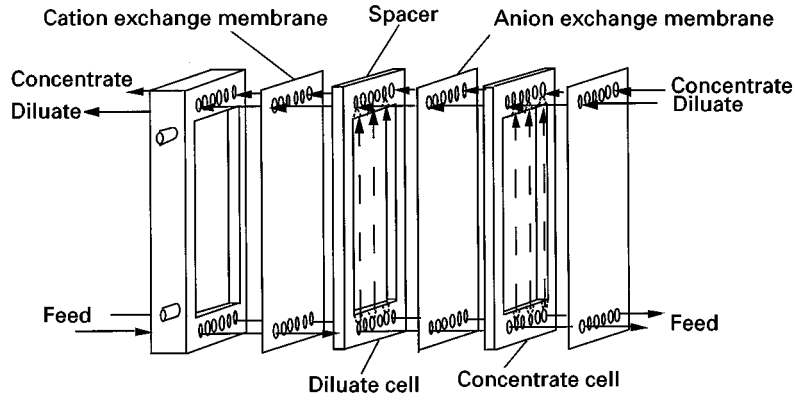


**Figure 4** Exploded view of an electrodialysis stack arrangement, indicating the individual cells and the sheet flow-type spacer, also containing the manifolds for distribution of different flow streams.

**Figure 4**. The membranes are stacked between electrodes in such a way that the flow streams are kept separate. The gaskets that separate the membranes contain manifolds to distribute the process fluids to the different compartments. The supply ducts for the diluate and the concentrate are formed by matching holes in the gaskets, in the membranes, and in the electrode cells. To minimize the resistance of the aqueous solution, the distance between the membrane sheets is made as small as possible and is normally between 0.5 and 2 mm in industrial electrodialysis stacks. In an industrial electrodialysis system, 200–1000 cation and anion exchange membranes are installed in parallel to form an electrodialysis stack with 100–500 cell pairs. Spacers between the individual membrane sheets support the membranes and provide mixing of the flow streams.

A proper electrodialysis stack design provides the maximum effective membrane area per unit stack volume and ensures uniform flow distribution through each compartment. The spacer screen should provide a maximum of mixing of the solutions at the membrane surfaces to reduce concentration polarization, but the pressure loss must be small.

### Process Design and Modes of Operation

The efficiency of electrodialysis in a given application depends greatly on the process, design and mode of operation. Two different operating modes are currently used: the first is referred to as unidirectional electrodialysis and the second as electrodialysis reversal.

A flow diagram of a typical unidirectionally operated electrodialysis plant is shown in **Figure 5**. Feed solution pumped into the stack is converted to a diluate and a concentrate which are collected in storage tanks when the desired degree of concentration or depletion is achieved. To prevent the formation of free chlorine by anodic oxidation, the electrode cells are rinsed with a separate solution that

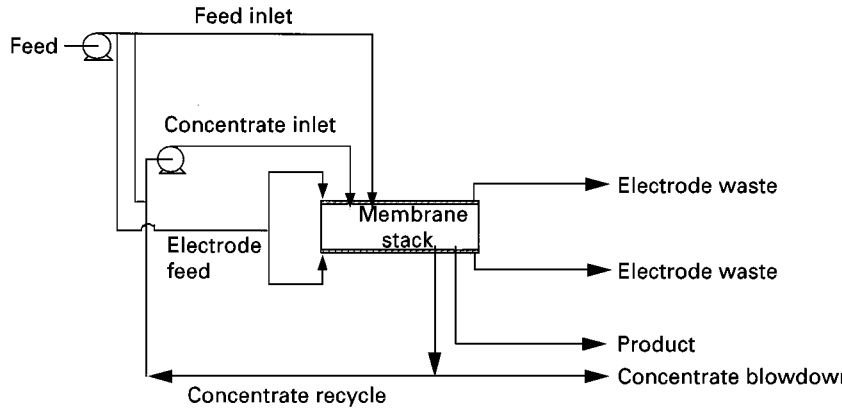


**Figure 5** Flow scheme of the unidirectional electrodialysis operating mode.

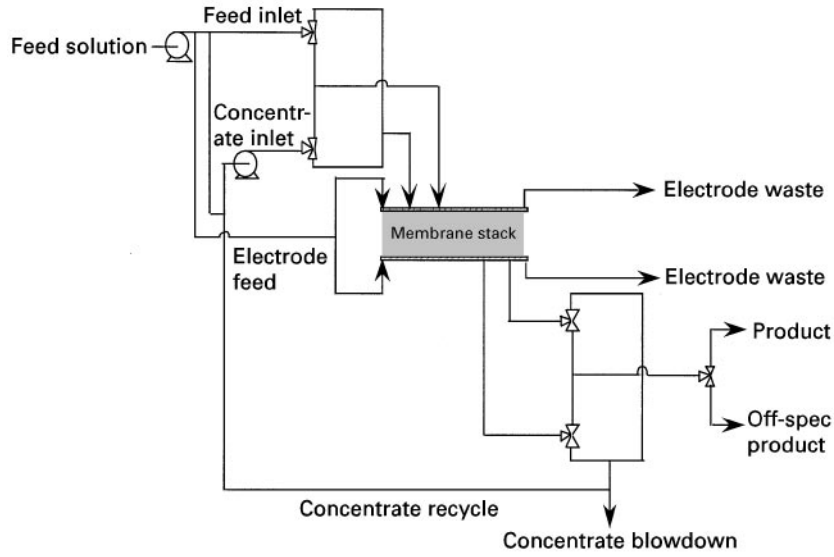


**Figure 6** Flow scheme of the electrodialysis reversal operating mode.

does not contain chloride ions. Unidirectionally operated electrodialysis plants are rather sensitive to membrane fouling and scaling and often require careful feed solution pretreatment and stack-cleaning procedures.

Membrane fouling and scaling can be greatly reduced by operating in the electrodialysis reversal mode. In this operating mode, the polarity of the current is changed periodically every few minutes to a few hours. Simultaneously, the hydraulic flow streams are reversed, as shown in **Figure 6**. The advantage of the electrodialysis reversal operating mode is that precipitates that are formed the concentrate cells are redissolved when the flow is reversed and these cells become the diluate cells. In the electrodialysis reversal operating mode there is a brief period when the concentration of the desalted product does not meet the product quality specification. Thus, a certain amount of the product will be lost to the waste stream.

## Electrodialysis Process Costs

The economics of an electrodialysis process are usually expressed as cost per unit product. These costs are the sum of fixed charges associated with amortization of the investment and operating costs such as energy and labour.

Investment costs include items such as the electrodialysis stacks, pumps, electrical equipment and membranes and are proportional to the required membrane area. The minimum required membrane area for a certain plant capacity is given by:

$$A = \frac{z\mathrm{F}Q\Delta Cn}{i\xi} \qquad [24]$$

The required membrane area for a given capacity electrodialysis plant is proportional to the amount of ions removed from a given feed solution and inversely proportional to the applied current density.

As indicated earlier, the applied current density should not exceed a certain limiting value. According to eqn [23] this value is proportional to the diluate concentration and the mass transfer in the boundary layers at the membrane surfaces. The mass transfer depends on the boundary layer thickness, which is a function of flow velocity. For given stack and feed solution properties, the limiting current density is given by:

$$i_{\mathrm{lim}} = {}^{\mathrm{bd}}C_{\mathrm{s}}\, a\, u^{\mathrm{b}} \qquad [25]$$

Here a and b are constants, the values of which are determined by a series of parameters such as the cell and spacer geometry, the solution viscosity and the transference numbers of ions in the membrane and the solution.

Eqn [25] shows that the limiting current density is proportional to the diluate concentration. However, the diluate concentration is changing during the desalting process from the concentration of the feed to that of the product. Thus, the limiting current density is decreasing along the flow path through the stack. The average limiting current density is proportional to the average concentration in the diluate cell and

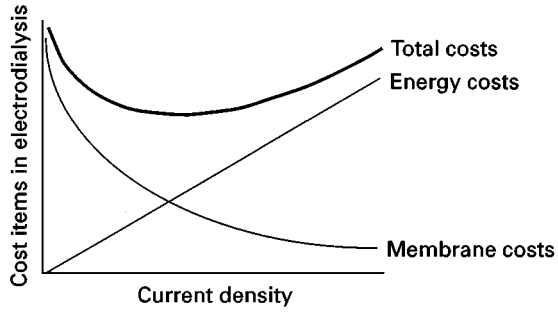


**Figure 7** Membrane, energy and total costs of the actual desalination process in electrodialysis.

given by:

$$\bar{i}_{\lim} = {}^{bd}\bar{C}_s \, a \, u^b = a \, u^b \frac{{}^{bd}C_s^o - {}^{bd}C_s^p}{\log \frac{{}^{bd}C_s^o}{{}^{bd}C_s^p}} \qquad [26]$$

Combining eqns [24] and [26] leads to:

$$A_{\min} = a' \frac{\log \frac{{}^{bd}C_s^o}{{}^{bd}C_s^p}}{{}^{bd}C_s^o - {}^{bd}C_s^p} \qquad [27]$$

The constant a′ is determined by the feed flow velocity, the stack design, etc.

The operating costs of an electrodialysis plant are mainly determined by the energy consumption which is the sum of the electrical energy required for the ion transfer and the energy necessary for pumping the solution through the stack, as indicated in eqns [17] and [18]. The energy required for the desalting process is a function of the feed solution concentration. The pumping energy depends on the flow velocities in the stack.

It should be noted that, according to eqn [12], the energy costs increase with increasing current density, while the required membrane area decreases with increasing current density. Thus the total desalination cost – which is the sum of capital, energy and operating costs – will reach a minimum at a certain current density, as illustrated in **Figure 7**, where the total cost of an electrodialysis process is shown schematically as a function of the applied current density.

## Applications of Electrodialysis

Electrodialysis is mainly used to desalinate saline solutions such as brackish water. But other applications such as the treatment of industrial effluents, demineralization of whey and deacidification of fruit juices are becoming increasingly important. In Japan, electrodialysis is also used in the production of table salt from sea water.

### Desalination of Brackish Water by Electrodialysis

In terms of installed plant capacity, the most important application of electrodialysis is the production of potable water from brackish water. Here, electrodialysis competes directly with reverse osmosis and multistage flash evaporation. For water with a relatively low salt concentration (less than 5000 p.p.m.), electrodialysis is generally considered to be the cheapest process. Another significant feature of electrodialysis is that salts can be concentrated to comparatively high values without affecting the economics of the process severely.

### Production of Table Salt

In the production of table salt from sea water, electrodialysis is used to concentrate sodium chloride up to $200\,g\,L^{-1}$ prior to evaporation. This application is developed and used nearly exclusively in Japan. Key to the success of electrodialysis in this application has been the development of membranes with a preferred permeability of monovalent ions.

### Electrodialysis in Waste Water Treatment

Treatment of metal ion-contaminated rinse waters produced in electroplating operations is an important application of electrodialysis. Complete recycling of the water and the metal ions can be achieved in favourable cases. A disadvantage, however, is that in electrodialysis only ions can be removed from a feed stream. Uncharged components that are also present in the rinse waters cannot be recovered.

Dump leach waters containing heavy metal ions have also been successfully treated by electrodialysis. The removal of nitrate from drinking water by electrodialysis is an application that seems to be competitive to processes such as ion exchange or reverse osmosis.

While in most of these applications the average plant capacity is considerably lower than that in brackish water desalination or table salt production, there is also a significant number of large plants installed for the treatment of refinery effluents and cooling-tower waste streams.

### Concentration of Reverse Osmosis Brines

Often the disposal of large volumes of brine obtained in reverse osmosis plants is difficult and further concentration is desirable. Because of the osmotic pressure, the brine concentration cannot exceed a certain value in reverse osmosis. A further

concentration, however, may be achieved at reasonable cost by electrodialysis.

#### Electrodialysis in the Food and Chemical Industry

Several applications of electrodialysis in the food industries, such as the demineralization of cheese whey, have considerable economic significance and are well established today. Other applications, such as the deashing of molasses or de-acidification of fruit juices, are still in an experimental stage. In the chemical industry electrodialysis is used for the desalination of protein, dextran or sugar solutions. Here, electrodialysis is often in competition with other separation procedures such as dialysis and solvent extraction. The separation of organic acids is an application of electrodialysis that is of interest to the pharmaceutical industry.

#### Production of Ultra Pure Water

Electrodialysis is now being used for the production of ultra pure water for the semiconductor industry. By combining electrodialysis with mixed-bed ion exchange resins, deionized water is obtained without a chemical regeneration of the ion exchange resin. The process has been commercialized recently.

## Conclusions

Electrodialysis has a long and proven history in the desalination of brackish waters. However, new applications in waste water treatment as well as in the food and the chemical industry are becoming more and more important. There are still a multitude of problems to be solved. Some are related to the properties of the membranes and the process design, while others are caused by the lack of application know-how and practical experience.

## Further Reading


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DropBooks

# Filtration

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## Introduction

Filtration is a key processing operation in the pharmaceutical, chemical and cosmetic industries. For example, filtration may be necessary to clear process solutions before analysis or as process step in manufacturing or in the sterilization of process solutions. Analytical testing requires only laboratory-scale filtration and is usually performed by a variety of membrane types depending upon the application. Filtration in manufacturing requires large-scale filtering in engineered devices called membrane modules or cartridges.

## Filtration Mechanism

Filtration is a mechanical phenomenon, which is sometimes aided by chemical manipulations of the filtration medium to make it more efficient. In any case, a driving force across the filter media is required. The following methods can be used to generate this driving force:

- Vacuum
- Pressure difference
- Centrifugal force
- Gravity pull
- Concentration difference
- Electrical potential difference
- Temperature difference
- A specific chemical attraction–repulsion